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ELECTRIC CONDUCTION OF COMPOSITE TITANIUM-CONTAINING COATINGS ON VITREOUS ENAMEL SUBSTRATES

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It is demonstrated that the main factor determining the high conductivity of heat-treated titanium-bearing phosphate coatings is the decrease in the resistivity of oxide films on the surface of titanium particles.

Resistive composite materials which do not contain precious metals are of interest for the development of film electric heaters. The main element of a film electric heater is the current-conducting coating formed on a dielectric substrate (glass, ceramic, or metal with an enamel insulating layer). Metal powders, in particular, titanium, are used as fillers in the production of inorganic conducting coatings, and glass or phosphates binders (USSR Author's Certificate 514783, 1422990) are used as binding agents. The conduction mechanism of these composite materials has not yet been sufficiently investigated.

There is currently no comprehensive theory of electric conduction of composite current-conducting coatings. The principal concepts are the contacting theory and the tunneling theory. The first concept accounts for the electric conduction in conducting composites by the formation of a chain structure of the conducting filler particles which are dispersed in the binder, and the second concept ascribes it to the conductivity of the conducting filler particles through the binder layer. In the cases where the vitreous binder is a semiconductor, the conduction mechanism is even more complicated [2].

The present paper investigates the conductivity specifics of titanium-bearing phosphate coatings formed on a vitreous enamel substrate.

The experimental coatings were produced using calcium hydride titanium powder of grade PTOM (TU 14-1-3086-86) with particle size below 40 μm and aluminochromium phosphate binder (ACPB) with molar ratio of

$\text{P}_2\text{O}_5 : (\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3)$ equal to 2.3 – 3.2 (TU 6-18-166-83). The slip was deposited on steel samples which had been previously coated with the insulating vitreous enamel 12p.

The resistance of the experimental coatings was measured using a combined instrument (Shch-4300 and E6-10). The silver layer burned into the dielectric substrate served as the electrodes.

The typical variation curves of the surface resistivity of conducting surfaces in heating (up to 400°C) and cooling are shown in Fig. 1. It can be seen that as the temperature increases, the resistivity significantly decreases (by several orders of magnitude). The high resistivity values of the dried coatings are easy to understand, considering that the outer surface of the initial titanium powder particles is covered by an extremely thin oxide film [3] which apparently persists in the stage of being mixed with the ACPB and determines the high resistivity of the coating.

It can be assumed that the conduction of coatings before heat treatment is implemented via the binder, i.e., the ACPB, and is of ionic nature. According to the data in [4], the presence of ionic conduction can be determined by the components which comprise the ACPB. As the temperature increases to 80 – 100°C, the ionic conductivity grows, and at a temperature of 100 – 120°C, when the binder loses the remaining free water, the coating resistivity increases slightly. With a further increase in the temperature, a smooth decrease of the coating resistivity is observed. The temperature dependence curve of the resistivity of the coating based on titanium and the ACPB exhibits a slight peak related to the eutectoid transformation of titanium hydride which was present in the initial powder in a small amount. In heating up to

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400–600°C, the surface resistivity decreases to a few units ($2.5 \Omega \cdot m$).

Cooling of samples to room temperature results in a slight linear increase in the coating resistivity proportional to the temperature resistance coefficient. This points to the fact that the sharp decrease in the sample resistivity under heating is determined not by the temperature dependence of the resistivity but by the modifications of the coating structure. A similar type of dependence of the resistivity on the heat treatment temperature is observed when the coating is deposited on a quartz glass substrate, which testifies to the fact that the ratio between the substrate and the coating TCLEs has little or no effect on the sample resistivity.

The obtained results do not give a unique explanation of the reasons for the substantial decrease in the resistivity of conducting coating when heated. Judging from the increase in weight registered by the differential thermal analysis, slow oxidation of the powdered titanium heated in air begins at 280°C [5]. The emergence of a slight quantity of titanium oxide (rutile) is registered in the x-ray diffraction patterns of samples heat-treated at temperatures above 700°C. The oxidation of titanium must be accompanied by an increase in the thickness of the oxide film on the powder particles and thus should increase the resistivity of the composite, and yet the experimental data testify to its substantial decrease.

It is known that the conductivity of composite materials significantly depends on the number of inter-particle contacts. The addition of the ACPB to the filler produces the effect of constriction resulting from the tendency to spontaneous compression under heat treatment. As was noted in [6], the volume of the binder in polymerization is reduced by about 15%. Consequently, as the water is removed in the drying stage, compaction occurs in the contact zone between the particles, which probably involves partial disintegration of the oxide film along the sharp facets of the grains. However, a decrease in the resistivity under heating was also observed in a model coating consisting of titanium powder suspension in distilled water which was applied to a vitreous enamel substrate. The resistivity of this coating after drying in air was 6.3×10^{-7} to $7 \Omega \cdot m$, which is of approximately the same order as that of the coating based on titanium with 10 wt.% ACPB ($1.6 \times 10^8 \Omega \cdot m$). In heating from 20 to 400°C, the resistivity of the titanium coating (which is, in fact, titanium powder) decreases to $4.0 \Omega \cdot m$ and is determined only by the variation of the resistivity of the film on the surface of the metal particles.

The observed decrease in coating resistivity in heating is caused by the modifications in the structure and composition of the oxide film in the contact zone between the titanium particles and the disturbance of its stoichiometry, which is probably due to the mutual diffusion of the titanium atoms into the oxide film crystal lattice and the oxygen ions into the metallic titanium lattice. As the stoichiometric composition

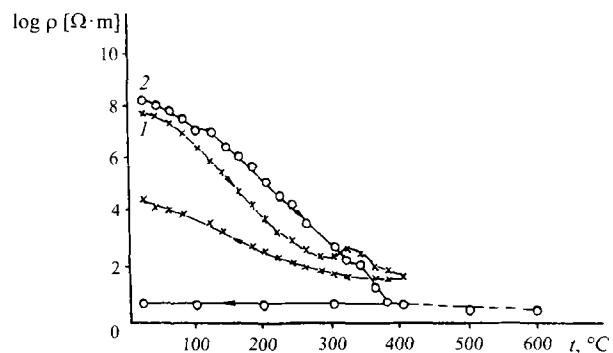


Fig. 1. Variation of surface resistivity of coatings in heating and cooling: 1) coating based on powdered titanium suspension in water; 2) coating consisting of 90% titanium and 10% ACPB.

of the oxide film (TiO_2) deviates toward oxygen deficit, its resistivity increases significantly [7]. The relationship between the resistivity variation and the state of the oxide film on the surface of titanium grains is supported by the fact that when samples of the model titanium coating preliminarily heated to 400°C are kept in air for a long period (a few months), the resistivity of the coating slowly increases from 4.0 to $10^6 \Omega \cdot m$.

Thus, comparing the temperature dependences of the resistivity of the composite coating based on powdered titanium and the ACPB and the model coating based on powdered titanium suspension in water, and considering the data on titanium oxidation, it may be inferred that the main factor determining the high conductivity of heat-treated coatings is the decrease in the resistivity of the oxide films on the surface of titanium particles.

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